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Abstract. The relative current noise power spectral density $S = S_I(f)/I^2$ observed in organic semiconductors exhibits a maximum at the *trap-filling transition* between the *ohmic* and the *space-charge-limited-current* regime. The electrostatic conditions determining the crossover from ohmic to space-charge-limited transport at the *trap-filling transition* are here discussed. These arguments shed light on the need to adopt a *percolative fluctuations* model to account for the competition between insulating and conductive phases as the voltage increases.

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INTRODUCTION

The phenomena underlying carrier transport in disordered solids continue to raise the interest of the scientific community. $f^{-\gamma}$ noise is an almost universal phenomenon observed in such systems. In spite of the intense research effort, a general agreement on the origin of such noise has still to be achieved. In homogeneous conductors, the relative spectral density of noise is independent of the voltage V when the Ohm law holds. Under the same assumptions, at fixed voltage, an increase (respectively decrease) of the free charge carrier density n results in a monotonic decrease (respectively increase) of the relative fluctuations. The relative noise power spectral density of the current can be directly equated to the relative noise power spectral density of the charge carrier density as $S = S_I(f)/I^2 = S_n(f)/n^2$. Under the assumption of independent fluctuations of n, it is $\langle \delta n^2 \rangle \propto n$ and thus $S \propto f^{-\gamma}/n$.

This simple law is rarely found in inhomogeneous systems. The application of an electric, magnetic or photon field causes the current paths to be randomly modified by acting on the different conductive properties of the coexisting phases and interfaces. Similar phenomena are observed in ferroelectrics, polymers and copolymers, superconductors and magnetic semiconductors, island-like metallic films, carbon-wax mixtures, polycrystalline semiconductors only to mention a few examples [1, 2]. The common feature shared by these systems is the transformation undergone by the conduction paths upon variation of a control parameter in an otherwise quasi-homogeneous conductive struc-

ture. The modification of the conduction paths - upon the external bias - results in a current flowing according to a two-phase percolation process arising from the competition between metallic and insulating components. Current fluctuations have been employed to probe the electronic properties of inhomogeneous systems. Both the amplitude and the spectral characteristics of the noise are indeed extremely sensitive to the dynamics of the current paths upon the external excitation [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. One important aspect is that the behavior $S \propto f^{-\gamma}/n$ for homogeneous conductors, is not observed in inhomogeneous systems. Relative noise power spectral densities changing with the voltage have been indeed reported. Furthermore, at constant voltage values, the $1/n$ dependence of the relative noise lacks to occur when the charge carrier density n is changed. $1/n$ deviations are obtained when polycrystalline photosensitive materials are irradiated. The photon flux, preferentially and disorderly, increases the conductivity of the regions where photosensitive defects are located, resulting in the formation of coexisting paths having different conductivities [4, 5]. Another feature often observed in inhomogeneous systems is the non-gaussianity of the noise traces. All the mentioned issues are diverse aspects of an unique problem: the charge carrier transport takes places across narrow conductive paths, with a volume which is only a small part of the whole conductor and with always less "fluctuators" involved in the stochastic process.
$f^{-\gamma}$ fluctuations have been recently observed in thin films of pentacene and tetracene. Pentacene and tetracene are small-weight organic molecules formed respectively by five, $C_{22}H_{14}$, and four, $C_{18}H_{12}$, benzene-like rings [6]. The study of noise in organic insulators is interesting at least for two reasons: (i) a complete understanding of the mechanisms underlying the charge carrier transport in organic small chain and polymers has not yet been fulfilled and still many unsolved issues remain; (ii) the deployment of organic and polymeric materials in the electronic industry requires a detailed insight into the dynamics other than into the time-averaged properties of the charge carrier transport [15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. We have reported that the relative power spectral density $S(f)$ observed in polycrystalline polyacenes is consistent with steady fluctuations of thermally generated and of injected charge carriers, respectively in *ohmic* and in *space-charge-limited-current* (SCLC) regime. The relative noise suddenly increases at the *trap filling* region at intermediate voltage. The peak has been estimated within a simple percolation model of the fluctuations as a consequence of the imbalance between empty and filled traps. In *ohmic* regime, the conductive component almost exclusively consists of thermally activated charge carriers n_{th} with the deep traps almost completely empty. In SCLC regime, the transport is dominated by the injected charge carriers n_{inj}, controlled by space-charge, with deep traps almost completely filled. The intermediate voltage region, *trap-filling regime*, is characterized by the coexistence of a conductive and an insulating phase, corresponding respectively to empty and filled traps, with deep traps almost completely filled. The system can be viewed as a two-components continuum percolative medium. The material, initially in the quasi-homogeneous ohmic phase, becomes populated by insulating sites as the voltage increases. The current paths become extremely intricate owing to the inhomogeneous distribution of trapping centers, whose occupancy randomly evolves as the Fermi level moves through the trap level. The system is in a strongly disordered state, due to the nucleation of insulating patterns inside the conductive medium. The relative noise intensity $S(f)$ of the system undergoing

the trap filling transition exceeds that of the same system when one of the two phases prevails. The increase of fluctuations has its origin in the greatly disordered distribution of local fields compared to the almost uniform distribution characterizing the ohmic and the SCLC regimes. The resistance R and the excess noise $S(f)$ observed in a percolative system are described by means of the relationships [27, 29, 30, 28]:

$$R = \frac{1}{I^2}\sum_{\alpha} r_\alpha i_\alpha^2 = \frac{1}{I^2}\sum_{\alpha} r_\alpha^{-1} v_\alpha^2 \tag{1}$$

$$S(f) = s_\Omega(f)\frac{\sum_\alpha i_\alpha^4}{(\sum_\alpha i_\alpha^2)^2} \quad , \tag{2}$$

where i_α and v_α are respectively the current and the voltage drop across the resistances r_α in the network. I is the total average current, $s_\Omega(f)$ indicates the noise spectral density in each conductive element of the network. The resistance R and the excess noise $S(f)$ progressively increase as the conductive matrix becomes sparse according to the relationships:

$$R \propto (\Delta\phi)^{-t} \tag{3}$$

$$S \propto (\Delta\phi)^{-k} \tag{4}$$

where ϕ represents the conductive fraction. t and k are critical exponents depending on the structure, composition and conduction mechanism (e.g. lattice, random void, inverted random void).

An expression of $S(f)$ in terms of physical observable depending upon the external drive has been worked out in [6]. During trap-filling, the conductive site fraction of the network is reduced proportionally to the free charge carrier density decrease caused by the increased number of trapped charge carriers. It is:

$$\Delta\phi \propto \frac{n - n_t}{N_v} \tag{5}$$

where n and n_t are respectively the free and trapped charge carrier densities, N_v is the total density of states, coinciding with the molecular density for narrow band materials as polyacenes. The Eq. (5) can be rewritten as:

$$\Delta\phi \propto \frac{n}{N_v}\left(1 - \frac{n_t}{n}\right) \tag{6}$$

It follows that the noise, exceeding the level that would be expected for an homogeneous conductor with comparable density of free charge, arises from the term $(1 - n_t/n)$, i.e. from the imbalance between free and trapped carriers. Assuming for simplicity a discrete trap level, it is $n = N_v \exp[-(E_v - E_F)/kT]$ and $n_t = N_t/\{1 + g^{-1}\exp[-(E_F - E_t)/kT]\} \simeq 2N_t \exp[(E_F - E_t)/kT]$, E_F being the quasi-Fermi level, g the degeneracy factor of the trap and the other quantities have the usual meaning [15]. The resistance R and the excess noise S diverge at the percolation threshold ϕ_c according to the relationships: $R \propto (\phi - \phi_c)^{-t}$ and $S \propto (\phi - \phi_c)^{-k}$. The percolation threshold ϕ_c and the onset of breakdown were obtained as a consequence of

additional traps progressively formed by bias or thermal stress. The increase of the trap density N_t enhances the unbalance between free and trapped charge carriers n_t/n [6, 7].

The system corresponds to a binary phase system where the transport is confined to narrower and narrower conductive paths worn away by larger insulating regions as the voltage increases. In the remainder of the paper we will add further insights into the percolative fluctuation model arguing on the relationships between thermal and injected charge carrier densities. These relationships will be then used to show that the observed behavior could not have been deduced as linear superposition of the fluctuations of the two diverse components demonstrating the evidence of the percolative mechanism of the transport. The puzzling phenomena related to transport in organic and polymeric material could be unraveled by an investigation accounting for the statistical properties, namely the fluctuations, of the charge carrier dynamics. Pure organic materials could be considered *perfect insulators*, i.e. materials that, under an applied voltage, carry a negligible current associated to the injection of charge carriers according to the mechanism known as Space Charge Limited Current (SCLC). The Space Charge Limited Current characterizes the emission from a thermionic cathode into vacuum and is analytically described by the *Child law*. Compared to vacuum, the description of the space-charge-limited current in solids requires to keep into account the complications arising from the electron-lattice interactions and by the unavoidable chemical impurities and structural imperfections. The onset of charge injection under SCLC conditions from the electrode critically depends on the presence of deep and shallow energy states related to the unavoidable defects at the metal-organic interface and in the bulk. The low-voltage region, with slope $l \approx 1$, corresponds to the *ohmic* regime, described by:

$$J_\Omega = q\mu nV/L \ . \tag{7}$$

The high-voltage region, with slope $l \approx 2$, corresponds to the trap-free space-charge-limited-current regime, obeying the *Mott-Gurney law*:

$$J_{\mathrm{SCLC}} = 9\varepsilon\varepsilon_0\mu\Theta V^2/8L^3 \tag{8}$$

where Θ is the trapping parameter and the other quantities have the usual meaning. The intermediate voltage region, the trap-filling region, is analytically described by the *Mark-Helfrich law* [15]. The current crossing the material under SCLC regime is carried by the injected carriers n_{inj}, depending on V according to:

$$n_{inj} = \frac{\varepsilon\varepsilon_0}{eL}\, V \tag{9}$$

The ohmic regime described by the Eq. (7) dominates up to a voltage, the threshold voltage V_t, where the injected free charge carrier density n_{inj} becomes comparable to the thermal concentration n_{th}. Furthermore, at V_t one can assume that the injected charges have completely filled the traps. This condition is expressed by the relationship:

$$n_{inj}(V_t) \approx N_t - n_t(V_t) \tag{10}$$

At the crossover from ohmic to SCLC regime, the charge carrier transit time $\tau_t = L^2/\mu V$ becomes comparable to the dielectric relaxation time $\tau_r = \varepsilon\varepsilon_0/en\mu$. The condition $\tau_t = \tau_r$ provides the value of the threshold voltage V_t :

$$V_t = \frac{N_t e L^2}{\varepsilon \varepsilon_0} \tag{11}$$

The sudden increase exhibited by the current at V_t can be estimated through the current change accompanying a doubling of the voltage. Therefore by taking $V = 2V_t$ and because of the proportionality of the injected charges to the voltage [Eq. (9)], the total injected charge can be assumed to double:

$$n_{inj}(2V_t) = 2n_{inj}(V_t) \quad . \tag{12}$$

Since, on average, the traps are completely filled at V_t, the additional charge n_{inj} must all appear in the valence band (respectively in the conduction band for electron conduction). The trap filling process is thus accompanied by a conductance change:

$$\delta G_t = \left(\frac{\partial G}{\partial V_t}\right) \delta V_t \propto n_{inj}(V_t) \quad , \tag{13}$$

that accounts for the current increase [31]. This relationship can be analytically obtained using the *regional approximation* to calculate the current change over the trap-filling region [15]. We will use the relationships (10-13) to argue on the need of the percolation picture for the current fluctuations observed at the trap-filling transition. The increase of the ratio n_t/n with V, i.e. the onset of the noise peak, can be directly deduced using the Eq. (9) and Eq. (10). At low bias, it is $n_t \ll n$ and thus the term $(1 - n_t/n)$ in Eq.(6) is close to 1. As the trap-filling region is spanned by varying the voltage the injected carrier densities increase with voltage, the ratio $n_t/n \to 1$ with the consequent divergence of the noise. If the transport process would occur in an homogeneous system, the increase of the total number of charge carriers n, due to the contribution of the injected ones n_{inj}, will result in a decrease of noise. The charge carrier trapping has the additional effect to increase the number of insulating region and forces the current flow to the narrower conductive paths. The dynamic evolution of the complex structure where the transport takes place is clearly deduced from the occurrence of a peak in the noise. It could not have been deduced simply from the $I-V$ characteristics, that, as we have discussed above, will lead to the opposite conclusion.

Let us now address the limits and the extent of validity of the model described above and in [6, 7]. The relationships (1-4) apply only to the ohmic and trap-filling region of the $I-V$ characteristics where the noise is mostly due to charge carrier fluctuations. When the trap-free SCLC regime is fully achieved, the current is determined by the injection of charge carriers from the cathode. The noise is originated by fluctuations of the emission probability over the metal-organic potential barrier. The mechanism is thus analogous to the shot noise $S_{\text{shot}} = 2eI\Gamma$, observed in vacuum tube or solid state junctions, where the space charge, built-up in the interelectrode region, produces a negative feedback effect on the fluctuations [6]. Such a noise mechanism could indeed explain the decrease of the relative fluctuations observed when the trap-free space-charge-limited conduction is fully achieved. In organic semiconductors, a more complicated relationship than $S_{\text{shot}} = 2eI\Gamma$ should be expected, due to the correlation between hopping events. The transport through a two-component disordered system made of ohmic and SCLC elements is not

exactly described by the Eqs.(1-4). In fact these expressions hold for a metal-insulator mixture with the insulator carrying no current at all [29] or with a matrix with two different sets of conductors [30]. The two conductors have different ohmic conductivities and the fluctuations arise from an ohmic mechanism in the two sets of conductors. As opposed to the situations considered in [29, 30], the analytical treatment of the fluctuations in a SCLC disordered conductor would require to take into account the different mechanisms of noise occurring respectively in the ohmic and in the SCLC phase of the matrix.

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